

UNPUBLISHED DATA

FINAL REPORT FOR NASA GRANT NsG-225-61

by Paul W. Gast, Senior Investigator

The essential accomplishments arising from work supported by the grant are summarized in a preliminary manuscript which is attached to this report.

The personnel supported by the grant included Paul W. Gast as senior investigator and M.R. Coscio as a part-time research assistant.

In addition to results described in the manuscript, several other meteorite-related efforts were partially supported by the grant. A seminar which met twice a week dealing with meteorites and related topics was held during the winter quarter of 1963. This was attended by 12-15 students both from the Department of Geology and Geophysics and from the School of Physics.

Some work on the mineralogy and texture of the meteorite Estherville was started. The preliminary results show that this meteorite contains a variety of pyroxenes, one of which (peckhamite) is unlike any terrestrial sample. Further support for this work will be requested by other investigators.

The results included in the manuscript which follows were presented at the 44th Annual Meeting of the American Geophysical Union, April 17-20, 1963. The published abstract is reproduced below.

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Rb, Sr, Ba, and Isotopic Composition of Sr in
Some Stone Meteorites

The abundance of Rb, Sr, and Ba in isotopic composition of strontium has been investigated in three chondrites. All Rb and Sr contents were measured in duplicate or triplicate; isotope abundances were determined in quadruplicate. If previously reported Sr^{87} abundances in achondrites is taken as the initial abundance, ages for gray chondrite, Bruderheim, and enstatite chondrite, Hvittis, are $4.36 \pm 0.09 \times 10^9$ and $4.35 \pm 0.09 \times 10^9$ years, respectively, where $\text{Rb}^{87}\lambda = 1.47 \times 10^{-11}$. These ages are in excellent agreement with the previously reported mean of chondrites. Water-soluble and insoluble fractions as well as total meteorites were investigated for the enstatite chondrite Abee. The apparent age of total sample is $4.01 \pm 0.08 \times 10^9$ years. Results of the leaching experiment suggest that there has been some differential movement of Rb and radiogenic Sr^{87} subsequent to 4.35×10^9 years ago. Both the barium and strontium abundances in the enstatite chondrites appear to be significantly lower than those found in most other chondrites.

8/3/64

THE ISOTOPIC COMPOSITION AND THE AGE OF STONE METEORITES--II: THE ENSTATITE CHONDRITES

INTRODUCTION

In a previous paper I have reported isotopic and abundance data on a series of achondrites and normal chondrites. A number of additional measurements mainly on enstatite chondrites are presented in this paper. The experimental problems of adequate sampling and non-reproducible rubidium determinations which remained unsolved in the first report have been solved in this study.

EXPERIMENTAL IMPROVEMENTS

The experimental methods employed in this study are basically those described previously modified to include calcium and barium in the separation scheme and using Sr^{84} rather than Sr^{86} as a stable isotope tracer. Improved mass spectrometer techniques have also made possible more precise determinations of the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio.

Rubidium determinations in the previous study were not as reproducible as those made on terrestrial rocks and minerals. It was suggested that this was due to absorption of rubidium on the insoluble residue with ensuing unequal distribution of rubidium between aliquots. This hypothesis was investigated by adding a Cs^{137} tracer to one of the solutions having a typical insoluble residue. This residue was centrifuged off and counted in a scintillation counter with a 10-kilovolt window. More than half of the original Cs^{137} appear in the residue. Even after washing with 5cc. of 2.5 NHCl , the residue contained

approximately 20% of the Cs^{137} . We infer from this that rubidium may be similarly retained in smaller amounts. This experiment confirms the suggestion made in my earlier work that rubidium could not be reproducibly determined, because the insoluble residue could not be evenly distributed between two aliquots.

In the work reported in this paper this difficulty has been overcome by adding the Rb^{87} tracer directly to the total sample.

Uncertainties in the abundance of strontium due to an inability to measure isotope ratios with an absolute accuracy better than $\pm 2\%$ were a major contribution to the overall uncertainties in calculated Rb-Sr ages in my earlier report. This uncertainty is almost entirely due to isotope fractionation during analysis of a strontium sample. In order to overcome these difficulties and in order to shorten the overall procedure, strontium was determined by means of a Sr^{84} tracer rather than a Sr^{86} tracer. With a proper choice of the amount of tracer to amount of sample strontium, the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio and the $\text{Sr}^{86}/\text{Sr}^{88}$ ratio may be determined on the same strontium sample mixed with the Sr^{84} tracer. Thus the isotope dilution runs may be corrected for isotope fractionation in the mass spectrometer and isotope composition and concentrations may be determined on a single mass spectrometer run. There is thus no need for aliquoting the sample either in the solid or in solution. Thus, all concentrations and the isotope composition of strontium are determined on the same material. Finally, the amount of sample which is consumed is reduced by a factor of two. A derivation of uncertainties in strontium concentrations and strontium isotope compositions arising in this method is given in Appendix I. The rather time-consuming calculation of isotope ratios and concentrations were made by successive approximations where the first approximation included no fractionation

correction. This calculation was programmed for a digital computer. The program is reproduced in Appendix II.

Chemical separations of strontium were carried out as described previously. This procedure was extended to include barium by elution with 6.2 N HCl after strontium had been removed from the cation exchange. A composite elution curve for several separations is given in Figure 1. Alkali metals were separated in two ways: (1) by precipitating with NaTPB prior to separation of strontium on an ion exchange column, and (2) by collecting potassium- and rubidium-containing fractions from the ion exchange process. The latter procedure was rejected because the alkali fractions were usually not pure and also because the position of rubidium and cesium could not be reproduced from run to run. It was found that in the presence of high iron concentrations, cesium is not retained on the ion exchanger in the same way as it is in dilute solutions. In the presence of iron much of the cesium came off the column along with iron in advance of potassium and rubidium. The most reproducible method of alkali metal separation in our experience is to precipitate alkalies along with 5 to 10 times as much NH_4^+ included as a carrier, using tetraphenyl boron. This precipitate was decomposed with HClO_4 and HNO_3 and heated to fumes of H_2SO_4 with a few drops of H_2SO_4 . The alkalies along with contaminating elements were then heated to red heat in a platinum dish and extracted with distilled water to separate alkalies from aluminum, iron, and magnesium, which are converted to insoluble oxides during the heating.

Mass spectrometric techniques were also substantially improved during the course of this study mainly by the introduction of a dual filament

source and later by use of an expanded scale in the recording system. The filament design is shown in Appendix III. Raw $\text{Sr}^{88}/\text{Sr}^{86}$ ratios determined on the single and dual filaments are compared in Figure 2. A nearly three-fold improvement in the precision of $\text{Sr}^{88}/\text{Sr}^{86}$ measurements results from this modification. In addition the dual filament arrangement yields higher ion currents for a given amount of sample. This is especially true for barium and calcium.

DESCRIPTION OF SAMPLES

Details of the meteorite samples used in this study are shown in Table 1. The St. Marks and Indarch samples consisted of single chips weighing about 7 grams. All of the available sample for both of these specimens was ground in a steel ball mill (Spex Model No.8200 Mixer Mill) without preliminary cleaning. The Hvittis sample consisted of a chip broken from a 150-gram slab. The Abec sample consisted of a small slab sawed from the end of a 1" x 1" prism. This slab included about equal amounts of matrix and fragments. A photograph of the prism end from which the sample was removed is shown in Figure 3. The Bruderheim sample consisted of a whole individual weighing about 70 grams. It was ground in a diamonite mortar and pestle. The plagioclase sample was separated and kindly donated to us by Dr. R.E. Folinsbee.

RESULTS

New measurements made in this study are given in Table 2. The results on two experiments attempting to determine the abundance of alkaline earth and alkali metals in the water-soluble fractions are also included in this table. These experiments will be discussed further after concentrations of

individual elements are considered.

The rubidium concentrations determined on separate aliquots, Hvittis A₁ and A₂ are again in marked disagreement. The average of the two aliquot determinations is, however, in good agreement with the average of other determinations made by adding the tracer to the total sample. This is consistent with the earlier suggestion that the discordant rubidium results are due to unequal distribution of rubidium absorbed on the insoluble residue between the two aliquots. Duplicate rubidium determinations suggest that the error in a single rubidium determination is less than $\pm 2\%$. Duplicate strontium measurements suggest a similar uncertainty, e.g., four determinations on Bruderheim have a mean deviation of $\pm 2.1\%$. The standard error of the mean for these four determinations is thus about $\pm 1\%$ of the mean strontium concentration 11.12 ppm.

Blank determinations have been discussed in a previous paper (Gast, 1962). Additional blank measurements for 1.2 grams of meteorite sample made during the course of the work discussed here are as follows: rubidium-- .014 micrograms, .008 micrograms; strontium--0.10 micrograms; barium--0.33 micrograms. These blanks introduce no significant error into the results for rubidium and strontium given in Table 2. The rubidium blank is less than $1/2\%$ of the determined rubidium; the strontium blank is about 1% of the determined strontium. Isotopic compositions have been corrected assuming that the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the blank is 0.710. The isotope composition determined on "spiked" and "unspiked" strontium has been compared in three runs--Bruderheim B, Hvittis B and C, and Bruderheim Albite D and ABC. In all three cases the

$\text{Sr}^{87}/\text{Sr}^{86}$ ratio found in the two determinations is in excellent agreement. The mean deviation of the three pairs is 3 parts in 7500. This comparison suggests that the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio can be determined on the same strontium used to determine the strontium concentration with no loss in precision. Repeat determinations of the 87/86 ratio suggests that the reproducibility is well within ± 1 part in 700. The difference between Hvittis A and the remaining Hvittis samples may be due to a sampling heterogeneity. Run A was made on a 2-gram piece sawed from a larger specimen. The remaining runs were made on a finely ground powder of the larger specimen. The mean deviation of the last four determinations is .0004. Similarly the mean deviation of all runs on the Bruderheim sample is .0007. The standard error of the mean for these duplicate runs is, therefore, well below 3 parts in 7000. I will somewhat arbitrarily use an uncertainty of $\pm .0005$ for the mean $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of Hvittis, Bruderheim, and Bruderheim Albite.

The concentrations of potassium, calcium, and barium were determined for several of the samples investigated here. Barium concentrations are less precise than the strontium determinations, because the barium blank is both greater and less well-determined than the strontium blank. It becomes quite significant for the lowest concentrations. I have assumed that the blank in the barium determination is $0.3 \pm .2$ micrograms. Thus, the blank introduces an uncertainty of as much as 10% in the concentration of the lowest concentrations. Calcium was determined with a Ca^{42} tracer. Isotope ratios were determined with an accuracy of $\pm 1\%$ or better. These concentrations are accurate to at least $\pm 2\%$. Potassium determinations were made as previously described.

Isotopic fractionation results in an uncertainty of at least $\pm 2\%$ in the potassium concentrations.

A major objective of this study was the investigation of the alkaline earth metals in those meteorites classified as enstatite chondrites. It was possible to obtain suitable samples of four such meteorites. It has been observed (Dawson, et al., 1960; Mason, 1962) that the calcium in these meteorites must in large part be in the mineral oldhamite (CaS) or in $\text{Ca}_{(1-x)}\text{Mn}_x\text{S}$. Since these sulfides are water soluble, it should be possible to make a crude separation of the silicate and sulfide alkaline earths by treating the meteorite with H_2O . We have attempted to investigate the distribution of calcium, strontium, and barium between water-soluble sulfides and water-insoluble minerals in two meteorites, Abee and Indarch. The water-soluble fraction was obtained by heating a powder with distilled water at 50°C . with occasional stirring. The soluble fraction represents three successive leachings with 15 cc. of water for 45 minutes. The insoluble residue was separated from the leachate by centrifuging. A second experiment was carried out on Abee using a more intensive procedure. The leaching time was increased to 3 hours and the temperature of the water increased to 80°C .

Results of these experiments are shown in Table 2. Since no sample was lost in either of the two experiments, the concentrations given as soluble and insoluble ppm. should add up to the value determined for the total meteorite. The Abee experiments are in excellent agreement with each other in this respect. This is clearly shown in Figure 5. The Indarch results are not entirely consistent in that they do not plot on a straight line. Comparison with the Abee results

suggests that the rubidium or strontium content of the leached fraction is incorrect. The sum of both calcium and barium in the leached and unleached fractions is in good agreement with the calcium and barium content determined on the total sample.

The second leach experiment on the Abee sample shows that the amount of radiogenic strontium which can be removed is variable. This result suggests the possibility that rubidium as well as strontium is partly soluble. Since the amount of leachable calcium did not change, it appears that the leached calcium and strontium may not all originate in the same phases. In addition, the second experiment suggests that the water-soluble 0.4% calcium represents the entire water-soluble fraction, i. e., less than half of the calcium is contained in water-soluble phases.

The relative ease of the removal of the alkaline earth and alkali metals is summarized in Table 3. Calcium is quite clearly concentrated more in the soluble phases than any of the other metals.

DISCUSSION OF RESULTS

Discussion of the data determined in this study will be divided into two categories: (1) element abundances, and (2) geochronology.

The abundance of calcium in the bronzite and hypersthene chondrites according to the compilation of Urey and Craig, 1953, is 2.00% CaO. The average calcium content of the enstatite chondrites using Urey and Craig's data along with more recent analyses by Wiik, 1956, and Dawson et al., 1960, is 0.9% CaO. A statistical comparison of the two groups of data indicates that the difference is highly significant. The barium data of Reed et al., 1960,

similarly suggest a lower barium content for one enstatite chondrite than that found in a number of hypersthene and bronzite chondrites. The results of this study clearly support the observation that the enstatite chondrites have lower alkaline earth metal contents than the normal chondrites.

In the present study this is best shown by the strontium concentrations. All of the results for the enstatite chondrites as well as all strontium concentrations determined for other chondrites by isotope dilution methods are shown in Figure 4. We note first that the range of strontium contents for the normal chondrites is remarkably narrow--much narrower than that observed for barium by Moore and Brown, 1963, even if their highest barium contents are excluded. Secondly, it is quite clear that the strontium content of the enstatite chondrites is about 30% lower than that of the normal chondrites. This is, of course, consistent with the previous observations for calcium and barium. It is not possible to make an equally good comparison for barium, but the few data that are available both from this study and the previous work of Reed, 1960, indicate that the barium content of the enstatite chondrites is significantly lower than that of the normal chondrites.

The calcium determinations for the Abee and Indarch made in this study are both higher than those previously reported by Dawson et al., 1960, and Wiik, 1956. This discrepancy could arise from inhomogenities in the meteorite samples, particularly in the case of Abee which is a polymict breccia. However, it should be noted that small amounts of calcium are hard to determine by wet chemical methods in the presence of large amounts of magnesium. It seems probable that the differences found here could also arise from errors

in the chemical analyses. The uncertainties stated for the new results are probably greater than they should be and it is very unlikely that the new results are too great by 10-25%. In any event, the calcium content of Indarch and Abee is still somewhat lower than the average value (1.5% calcium) for normal chondrites compiled by Urey and Craig, 1953.

This work as well as the study of Smales et al., 1964, indicates that the enstatite chondrites cannot be distinguished from normal chondrites on the basis of their alkali metal content.

The Bruderheim plagioclase sample analyzed here is the first separated plagioclase analyzed for alkali and alkaline earth metals. Modal analyses made by Duke, et al., 1961, indicate that this mineral makes up about 0.5% by volume of this meteorite, however, the normative plagioclase is nearly ten times greater by volume than that observed. The plagioclase abundance in other similar meteorites ranges from 5-10% (Michel, 1912). These facts suggest that the modal concentration of plagioclase determined by Duke, et al., 1961, is too low. If using the abundance of plagioclase is assumed to be greater than 5% by weight, the abundance determined in this study indicates that in the Bruderheim meteorite more than 50% of the potassium, rubidium, strontium, and barium are found in the plagioclase. Furthermore, the results obtained here indicate that there is very little fractionation of rubidium, strontium, or barium relative to potassium in plagioclase; i. e., rubidium is not enriched relative to strontium. Thus, there appears to be very little gained with regard to Rb-Sr dating in using plagioclase rather than the whole meteorite.

The geochronological results of this study are summarized in Figure 5. Some results from a previous study (Gast, 1962) are also shown in this figure. The new results are only partially consistent with previous results. Three of the five meteorites analyzed in this study, Bruderheim, Hvittis, and St. Marks, are in good agreement with the isochron age reported previously. The other enstatite chondrites and the separated plagioclase require further explanation.

The results for Bruderheim, Hvittis, and St. Marks meteorites are much more precise than those previously reported. It is thus possible to greatly reduce the uncertainty in the Rb-Sr age based on the apparently concordant samples. A least square analysis of the six concordant points plus the results for achondrites reported previously yields an age of 4.34 ± 0.1 A.E. for a Rb^{87} half life of 4.7×10^{10} years and $4.63 \pm .1$ A.E. for a Rb^{87} half life of 5.0×10^{10} . These ages bracket the age based on lead isotope ratios reported by Murthy and Patterson, 1962. A closer comparison of ages based on this method will require more accurate determinations of the Rb^{87} half life.

Figure 5 shows that the results for the Bruderheim plagioclase fall somewhat below the 4.34 A.E. isochron ($\lambda = 1.47 \times 10^{-11}$ years). Except for the one discrepant strontium determination, replicates for this sample are in good agreement. These replicate analyses allow a rather small uncertainty on both the $\text{Rb}^{87}/\text{Sr}^{86}$ ratio and the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio. Therefore, it is highly probable that the difference shown in Figure 5 is significant. It is possible that this discrepancy may be an indication of a partial redistribution of radiogenic Sr^{87} among the different mineral phases in this meteorite. The K-Ar ages

for three separated phases (plagioclase, orthopyroxene, and clinopyroxene) of this meteorite are clearly too young. They are, however, surprisingly concordant supporting the hypothesis that the apparent loss of argon is due to a late thermal event rather than loss by continuous diffusion. Such an event could be responsible for some redistribution of the radiogenic strontium as well as the loss of argon.

The discordant results for the two enstatite chondrites Abee and Indarch pose a more serious problem. The results on the total samples for these two meteorites are clearly discordant with the 4.35 b.y. isochron. The "age" based on the slope of the dotted line is 4.25 b.y. This is the time required to generate the present isotope composition if growth began with the achondritic $\text{Sr}^{87}/\text{Sr}^{86}$ ratio. Since we have already assumed that the achondrites were derived from a more primitive source (Gast, 1962) the cosmochronological meaning of this age is rather ambiguous. That is, the achondrites cannot be derived from both the normal chondrites and the enstatite chondrites. Both the texture of the Abee enstatite chondrites and the chemical differences between normal chondrites and the enstatite chondrites suggest chemical changes in the enstatite chondrites suggest chemical changes in the enstatite chondrites. The textural relations described by Dawson, et al., 1960, for example, iron replacing pyroxene in a chondrule; also, concentration of iron in the fragments with respect to the matrix of the breccia suggest that the iron reduction probably came after gross texture was established. It seems reasonable to suppose that removal of alkaline elements was associated with this event. The strontium isotope ratios and $\text{Rb}^{87}/\text{Sr}^{86}$ ratios determined in this study indicate

that this reducing event came significantly later than the formation of the achondrites. If the $\text{Rb}^{87}/\text{Sr}^{86}$ ratio in the Abee and Indarch chondrites was 0.9 (i. e., similar to that in the normal chondrites) from 4.63 by. (1.39×10^{-11} years) ago until the present ratio was established by removal of strontium during the iron reduction event, this interval would have to be 120 m. y. long in order to explain the observed differences.

The slope of the line drawn through the three Abee points need not have any cosmo-chronological significance. The first leaching experiment shows that some rubidium is removed by water. The second leaching experiment shows that the isotope composition of the leached strontium varies with the procedure, presumably because strontium is distributed among at least two water-soluble minerals. The slope of the dashed Abee line thus depends on the relative ease of removal of radiogenic strontium and rubidium as well as on the time when soluble rubidium phase and insoluble silicate phase were formed.

The explanation of the Indarch and Abee samples involves the early history of meteoritic matter and should thus be consistent with the history for this interval derived from both the xenon and argon isotopes. Kirsten, et al., 1963, have found that the K-Ar age for the Abee meteorite is 4.67 A.E. Jeffery and Reynolds, 1961, have presented strong evidence that the excess Xe^{129} has been formed "in situ." At first both of these observations seem inconsistent with the idea that iron reduction and removal of calcium, strontium, and barium took place more than 100 m. y. after achondrites were differentiated from a parent chondritic material. It is difficult to resolve the problem without much more information than is now at hand. First of all, it is very

important to know the conditions under which iron was reduced and alkaline earth elements removed before the question of gas retention during this event can be evaluated. Secondly, more information on the Xe^{129} and Sr^{40} bearing phases is needed. If the Abee meteorite underwent a chemical thermal event 100 m.y. after it was first formed, two somewhat improbable inferences must be drawn: (1) the Xe^{129} now in the meteorite was not separated from I^{129} during this event and (2) this meteorite contains excess Ar^{40} , perhaps in the form of "ambient argon" as Fish and Goles, 1962, have defined ambient gases.

Table 1. Description of Meteorites Used in This Study

Name	Classification	Form of Sample	Date of Fall	Source
Abee	enstatite chondrite	sawed prism	June 9, 1952	K.R. Dawson Geol. Survey of Canada
Indarch	enstatite chondrite	chip	April 7, 1891	G. Reed Chicago, Ill.
St. Marks	enstatite chondrite	chip	Jan. 3, 1901	Brian Mason New York
Hvittis	enstatite chondrite	slice	Oct. 21, 1901	Olavi Kouvo Helsinki, Finland
Bruderheim	hypersten chondrite	whole individual	March 4, 1960	R. Folinsbee Edmonton, Alberta
Bruderheim- Albite		powder		R. Folinsbee, Edmonton, Alberta

Table 2. Analytical Results

<u>Sample</u>		<u>Sr ppm.</u>	<u>Sr⁸⁷/Sr⁸⁶</u>	<u>Ba ppm.</u>	<u>Rb ppm.</u>	<u>K %</u>	<u>Ca %</u>
Bruderheim	A ₁	11.54	.7494	----	----	----	----
	B ₁	10.94	.7484	4.60	----	----	----
	B ₂	----	.7496	3.73	----	0.086	----
	C	11.15	.7493	3.76	2.759	----	----
	D	10.84	.7513	3.73	2.746	----	----
		11.12	----	----	----	----	----
Bruderheim Albite	A	71.0	.7497	34.4	26.0	0.805	----
	B	91.3	.7494	----	25.8	----	----
	C	91.5	.7482	----	25.7	----	----
Hvittis	A ₁	----	----	----	2.675	----	----
	A ₂	----	.7605	----	2.919	0.082	----
	B ₁	8.679	.7630	----	2.789	0.079	----
	B ₂	----	.7638	1.85	----	----	----
	C ₁	8.996	.7632	2.2	2.764	----	----
	C ₂	----	.7637	----	----	----	----
Abee	A	7.311	.7860	----	3.467	0.094	1.075
	sol.	2.298	.7229	0.30	0.19	0.0058	0.406
	insol.	5.066	.8144	2.70	3.230	----	0.632
	(soluble II)	----	.7342	0.67	----	----	0.371
Indarch	A	7.099	.7908	2.56	3.433	0.083	0.895
	sol.	1.144	.7390	< 0.2	0.296		0.360
	insol.	5.777	.8009	2.43	3.185		0.537
St. Marks		7.67	.7253	----	0.924	0.084	----
Moore County		----	.7015	21.6 ₊₁	----	----	----
Nuevo Laredo		----	----	44 ₊₂	----	----	----
Sioux County		----	----	25 ₊₂	----	----	----
Pasamonte		----	----	38 ₊₄	----	----	----

Table 3. Relative Solubility of Ca, Sr, Ba, Rb and K

	<u>Ca</u>	<u>Sr</u>	<u>Ba</u>	<u>Rb</u>	<u>K</u>
Abee I	39%	31%	10%	5.5%	6.2%
II	-----	-----	20%	-----	-----
Indarch I	40%	20%	<7%	8.7%	-----

TYPICAL ELUTION CURVES

FOR K, Rb, Cs, Ca, AND Ba

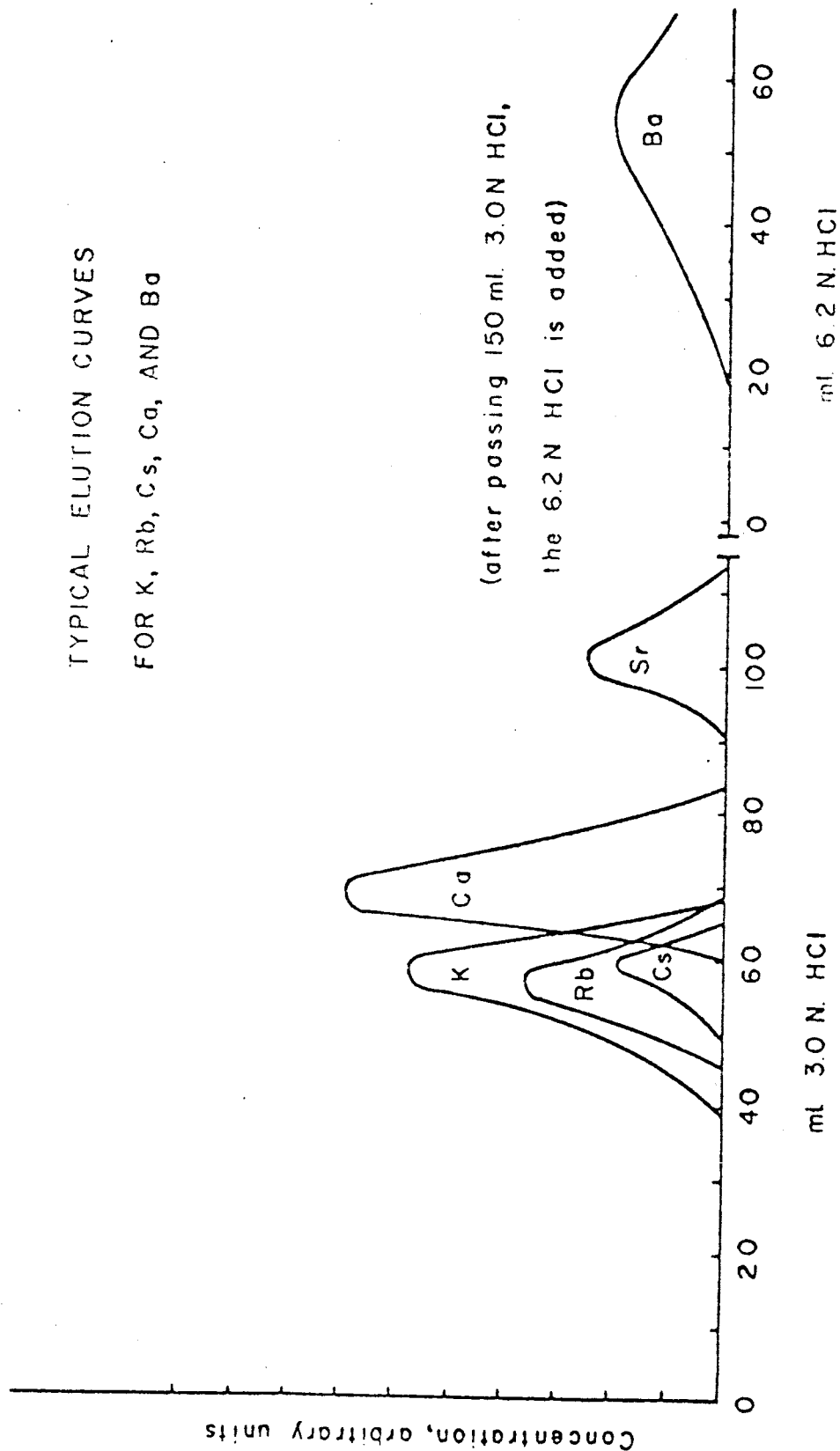
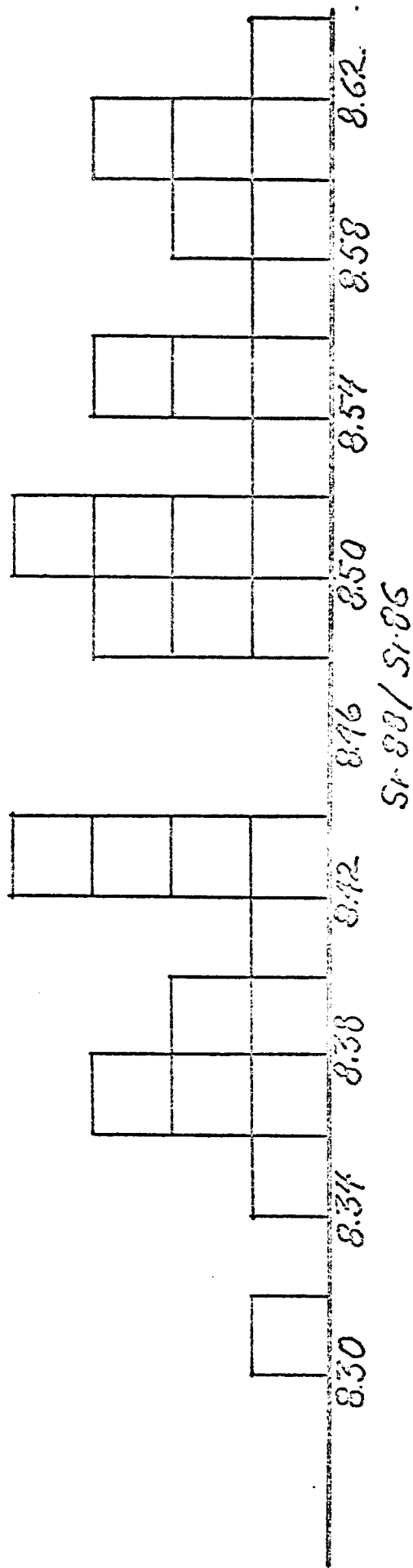


Figure 1. Elution curves for ion exchange column used to separate Ca, Sr, and Ba.

SINGLE FILAMENT SOURCE



TWO FILAMENT SOURCE

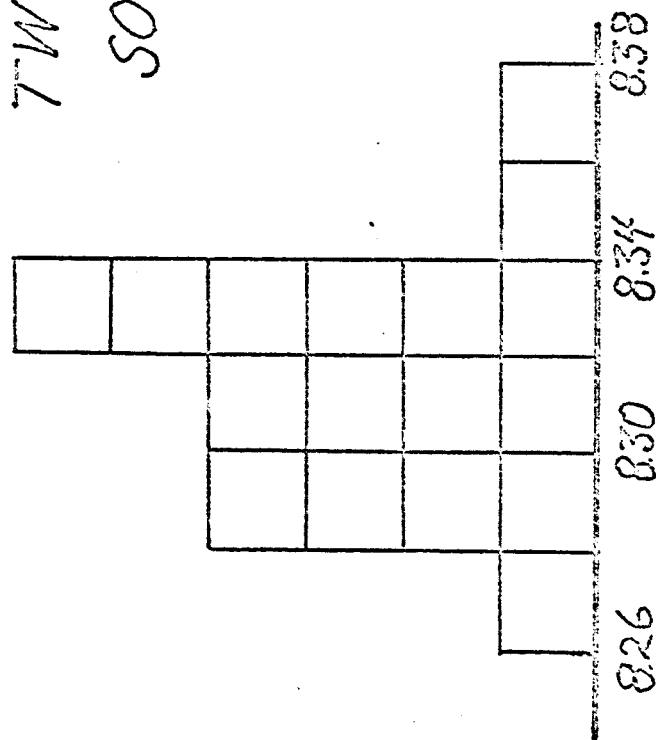


Figure 2. Comparison of Sr 88/Sr 86 ratio determined on single-filament and double-filament ion source.

Figure 3. Photograph of Abee meteorite section showing breccia inclusions rich in iron in an iron-poor matrix (5 times actual size).

Sr CONTENT OF CHONDRITES

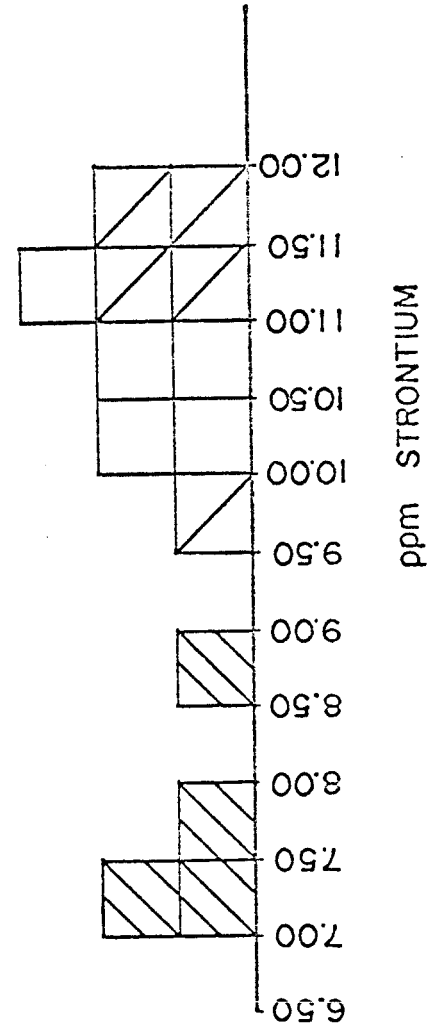
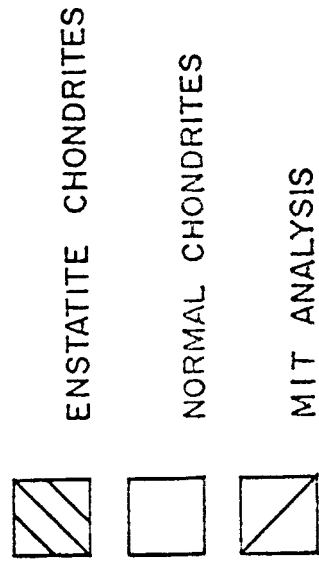


Figure 4. Distribution of strontium concentrations in chondritic meteorites.

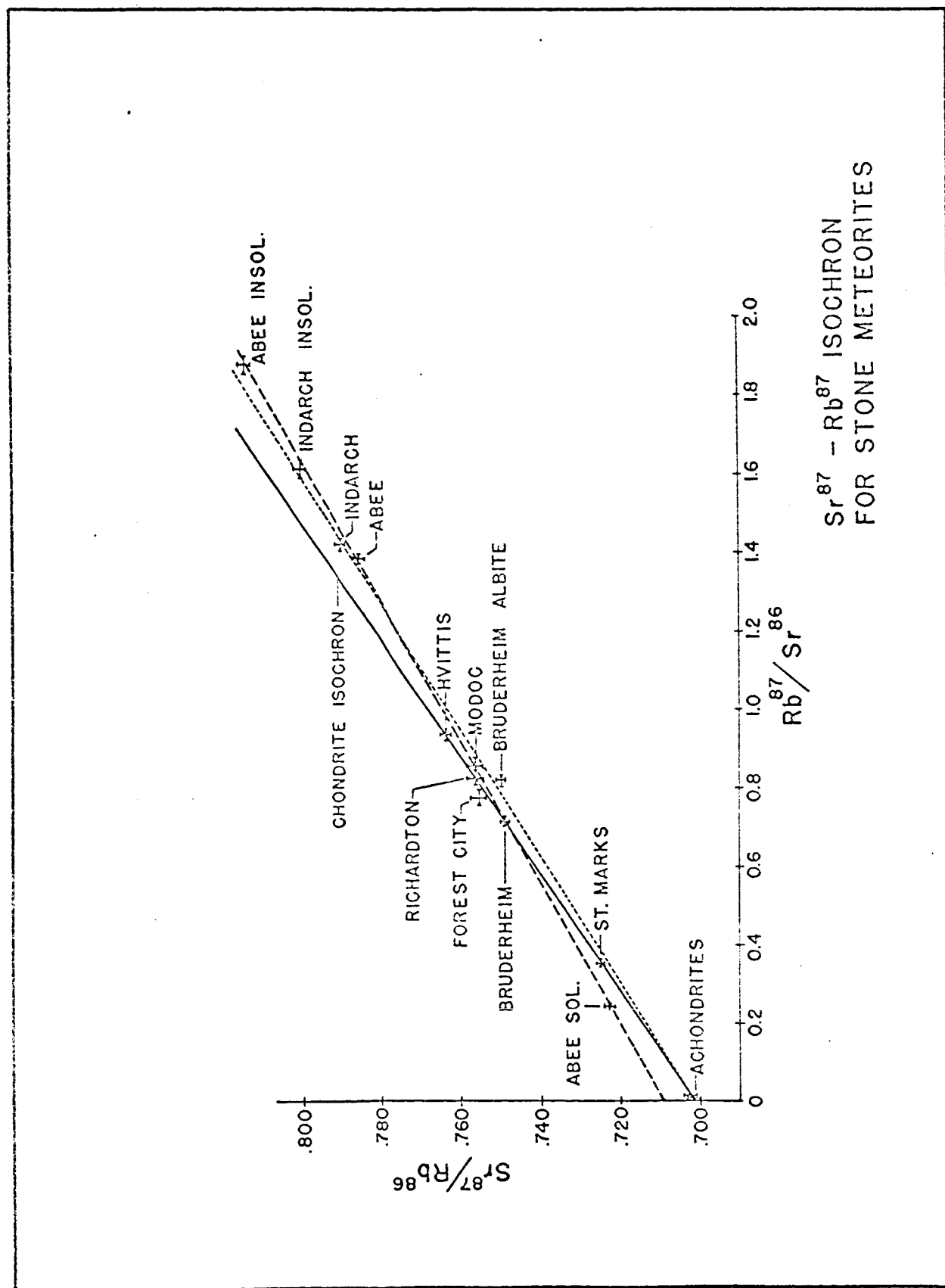


Figure 5.

APPENDIX I

A major limitation in the accuracy of strontium concentrations determined by isotope dilution method is the mass dependent isotope fractionation occurring during isotopic analysis. In the analysis of unspiked strontium it is possible to correct for this effect to the extent that the $\text{Sr}^{86}/\text{Sr}^{88}$ ratio is constant. In mixtures of enriched Sr^{86} isotopes and normal strontium this usually is not possible. However, if pure Sr^{84} is used as a tracer, the $\text{Sr}^{86}/\text{Sr}^{88}$ ratio may be used as an indicator of fractionation when the $\text{Sr}^{84}/\text{Sr}^{86}$ ratio is used to determine concentration. It should then be possible to measure variations in the Sr^{87} abundance as accurately on a sample consisting of a mixture of tracer and normal strontium as it is on an "unspiked" sample. The accuracy in the strontium concentration determined by this scheme is limited by the precision with which fractionation corrected ratios can be measured and by the accuracy of the tracer solution. Since the isotope composition of the tracer is determined just like that of the normal strontium, its isotope composition is also subject to uncertainties due to fractionation. Without some common or known isotope ratio it is not possible to correct the tracer for fractionation effects. In order to minimize the fractionation effects between the tracer and normal strontium, the tracer and normal strontium were analyzed several times under similar situations, i. e. similar consource configurations. The variations found in these replicate determinations suggests that the systematic difference in these strontium samples due to fractionation is less than 0.1% per mass unit. The effect of this uncertainty on absolute concentrations will be

evaluated below. Replicate for both rubidium and strontium tracer calibrations shown in Table A indicate that the uncertainty in tracer concentrations due to uncertainties in the purity of rubidium and strontium reagents used in making standard solutions is less than $\pm 1\%$.

DEFINITION OF SYMBOLS

R = isotope ratio

A = atomic abundance

C = micromoles of strontium

All ratios will be measured with respect to Sr^{86} . Thus, R_1 will designate $\text{Sr}^{88}/\text{Sr}^{86}$, $R_2 = \text{Sr}^{87}/\text{Sr}^{86}$, etc. A_1 = atomic abundance of Sr^{88} etc. Unprimed quantities refer to sample strontium, single primed quantities refer to the tracer and double primed quantities refer to mixtures of tracer and sample strontium. Finally, K is the fractionation factor per mass unit in percent. In the following analysis, $K = 0$ for normal strontium and mixtures, $K > 0$ for tracer. The effect of this non-zero K on C will be evaluated.

It is readily shown that C' is found from the following equation.

$$R_4'' = \frac{A_4 C + A_4' C'}{A_3 C + A_3' C'}$$

$$\text{or } R_4'' A_3 C + R_4'' A_3' C' = A_4 C + A_4' C'$$

by implicit differentiation

$$R_4'' A_3' \frac{\partial C'}{\partial K} + R_4'' C' \frac{\partial A_3'}{\partial K} = A_4' \frac{\partial C}{\partial K} + C' \frac{\partial A_4'}{\partial K}$$

In general
$$A_i = \frac{R_i}{\sum_j R_j}$$

thus
$$A_3' = \frac{R_3'}{\sum R_j' + K(2R_1' + R_2' - 2R_4')}$$

$$A_4' = \frac{R_4' (1-2K)}{\sum R_j' + K(2R_1' + R_2' - 2R_4')}$$

then
$$\frac{\partial A_3'}{\partial K} = \frac{-A_3' (2R_1' + R_2' - 2R_4')}{\sum R_j' + K(2R_1' + R_2' - 2R_4')}$$

$$\frac{\partial A_4'}{\partial K} = \frac{-2KR_4' - A_4' (2R_1' + R_2' - 2R_4')}{\sum R_j' + K(2R_1' + R_2' - 2R_4')}$$

thus by substitution and rearrangement

$$\frac{\partial C'}{\partial K} = \frac{C' \left(\frac{2R_4' - A_4'(2R_1' + R_2' - 2R_4')}{\sum R_j' + K(2R_1' + R_2' - 2R_4')} - R_4'' A_3' (2R_1' + R_2' - 2R_4') \right)}{R_4' A_3' - A_4'}$$

further, by substituting and rearranging

$$\frac{\partial C'/C'}{\partial K} = \frac{2R_4' - A_4'(2R_1' + R_2' - 2R_4') - R_4'' A_3' (2R_1' + R_2' - 2R_4')}{R_4'' R_3' - R_4' + R_4' 2K}$$

for the tracer used in this study

$$A_1' = 30.86$$

$$A_2' = 8.80$$

$$A_3' = 14.39$$

$$A_4' = 45.95$$

using these values and $R_4'' = 0.20$

$$\frac{\partial C'/C'}{\partial K} = 2.2$$

Thus, the 0.1% uncertainty in fractionation factor gives rise to a 0.22% uncertainty in the concentration of the tracer solution.

A more highly enriched tracer with the following abundances has been obtained recently. The uncertainty arising from fractionation using this tracer is substantially less. The isotope composition of this tracer is

$$A_1' = 83.3$$

$$A_2' = 3.88$$

$$A_3' = 1.29$$

$$A_4' = 11.5$$

$$\text{if } R_4'' = 0.5$$

$$\frac{\partial C'/C'}{\partial K} =$$

Table A. Replicate Calibrations of Tracer Solutions

Strontium-84 Tracer

0.1213 micromoles/ml	gravimetric
0.1230	reagent Sr solution 1
0.1229	reagent Sr solution 2
0.1237	specpure Sr solution 1
0.1226	specpure Sr solution 1
0.1222	specpure Sr solution 2

Rubidium-87 Tracer

0.0644 micromoles/ml	specpure Rb I solution 1
0.0644	specpure Rb I solution 1
0.0636	reagent RbCl solution 1
0.0636	reagent RbCl solution 1
0.0640	reagent RbCl solution 1
0.0638	specpure RbII solution 1
0.0638	specpure RbII solution 1
0.0636	specpure RbII solution 1

APPENDIX II

```

PROGRAM X
CALL LIMIT(5)
* P. GAST U OF MINN
* XEQ
* LIST8
* LABEL
CIDCALC
    DIMENSION RATIO (4),PERCEN(4),CONC(4),SAMRAT(4),SAMPER(4),ANS(4),
    1 ENUM(4),TRLS(4),TITLE(11),ISS(10)
1 WRITE OUTPUT TAPE 6, 10
10 FORMAT (1H1,24X,38HSTRONTIUM ISOTOPE DILUTION CALCULATION//10X,
155HTO PREPARE DATA FOR THIS PROGRAM, MAKE UP THE FOLLOWING
2/10X,6HCARD1,5X,15HMISS DIGITS 1011,5X,20HNAME COL S 11 TO 72.
3/10X,6HCARD2,5X,51HSPIKED RATIOS 88/86, 87/86, 86/86 AND 84/86 4F
49.4./10X,6HCARD3,5X,71HUNSPIKED RATIOS 1-4, SAMPLE WEIGHT IN GRAMS
5, INITIAL RATIO 87/86, 6F9.4/10X,6HCARD4,5X,66HTRACER CONCENTRATIO
6NS 88, 87, 86 AND 84 IN MICROMOLES, 36X, 4F9.8./)
    DO 3000 I = 1,4
        RATIO(I) = 0.
        PERCEN(I) = 0.
        CONC(I) = 0.
        SAMRAT(I) = 0.
        SAMPER(I) = 0.
        ANS(I) = 0.
        ENUM(I) = 0.
3000 TRLS(I) = 0.
    DO 3001 J = 1, 10
        TITLE(J) = 0.
3001 ISS(J) = 0
        TITLE (11)= 0.
        SUM = 0.
        A = 0.
        B = 0.
        C = 0.
        J = 0
        J1 = 0
        R4 = 0.
        READ INPUT TAPE 5, 11, (ISS(IS),IS=1,10),(TITLE(J),J=1,11)
11 FORMAT (10I1, 10A6, A2)
        WRITE OUTPUT TAPE 6,12,(ISS(IS),IS=1,3)
12 FORMAT(
/10X,40HCONTROL DIGITS
1ISS, NO PRINTING IF ZERO. /10X, 8HISS(1) = 12,2X,
2 25HWRITE SPIKED PERCENTAGES./10X,8HISS(2) = 12,2X,29HWRITE UNSPIK
3ED PERCENTAGES. / 10X, 8HISS(3) = 12, 2X, 96HWRITE TOTAL ISOTOP
4E 88, 87, 86 AND 84, TOTAL TRACER MICROMOLES, TOTAL MICROMOLES SAM
5PLE + TRACER, / 10X, 90HMICROMOLES UNSPIKED MATERIAL 88, 87, 86
6 AND 84, TOTAL UNSPIKED MICROMOLES OF SAMPLE, / 10X,
7 60HPLUS CORRECTED SPIKED RATIOS AND CORRECTED UNSPIKED RATIOS. )
        WRITE OUTPUT TAPE6,112,(ISS(IS),IS=4,10),(TITLE(J),J=1,11)
112 FORMAT (
10X, 12HISS(4
1 - 9) = 2I1, 3X, 4I1, 3X,11H(NOT USED.)/ 10X, 9HISS(10) = 12, 2X,
2 96HIF ZERO, ITERATE TWICE. IF ONE, ITERATE UNTIL CHANGE IN TRIAL
3 RATIO 88/86 IS LESS THAN 0.0001. /// 10X, 10A6, A2//)
        READ INPUT TAPE 5, 13, (RATIO(I), I = 1,4)
13 FORMAT ( 4F9.4)
        READ INPUT TAPE 5, 14, (SAMRAT (I), I= 1,4), WEIGHT, ONGRAT
14 FORMAT (6F9.4)

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Appendix II (continued)

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0  READ INPUT TAPE 5, 113, (CONC(I), I = 1, 4)
113  FORMAT ( 35X, 4F9.8)
    WRITE OUTPUT TAPE 6, 15, (RATIO(I), I=1, 4)
15   FORMAT ( /30X, 13HSPIKED RATIOS/10X, 7H88/86 = F12.6, 5X, 7H87/86
1    = F12.6, 5X, 7H86/86 = F12.6, 5X, 7H84/86 = F12.6 )
    WRITE OUTPUT TAPE 6, 115, (CONC(I), I = 1, 4)
115  FORMAT (                                     10X, 21HTRA
1    CER CONCENTRATIONS/ 10X, 4H88 = F15.7, 5X, 4H87 = F15.7, 5X, 4H86
2    = F15.7, 5X, 4H84 = F15.7//)
    WRITE OUTPUT TAPE 6, 16, (SAMRAT(I), I=1, 4)
16   FORMAT ( /30X, 15HUNSPIKED RATIOS/ 10X, 7H88/86 = F12.6, 5X,
1    7H87/86 = F12.6, 5X, 7H86/86 = F12.6, 5X, 7H84/86 = F12.6)
    WRITE OUTPUT TAPE 6, 116,                                WEIGHT, ORGRAT
116  FORMAT ( 10X,
1    16HSAMPLE WEIGHT = F12.6, 2X, 5HGRAMS, 5X, 25HINITIAL RATIO OF 87
2    /86 = F12.6//)
C    CALCULATION PART 1.
C    CALCULATE SUM OF RAW RATIOS.
    J = 2
5000  SUM = 0.
    DO 20 I = 1, 4
20   SUM = SUM + RATIO(I)
C    FIND PER CENT(I) FROM RAW RATIOS AND SUM.
    DO 21 I = 1, 4
21   PERCEN(I) = RATIO(I)/ SUM
    IF( ISS(1)) 1001, 1000, 1001
1001  WRITE OUTPUT TAPE 6, 2001, (PERCEN(I), I = 1, 4)
2001  FORMAT ( /10X, 18HSPIKED PERCENTAGES/
1     9X, 12HPERCENT 88 = F12.5, 5X, 12HPERCENT 87 = F12.5,
2     5X, 12HPERCENT 86 = F12.5, 5X, 12HPERCENT 84 = F12.5//)
C    CALCULATION PART 2.
C    FIND SUM OF SAMPLE RATIOS.
1000  SUM = 0.
    DO 22 I = 1, 4
22   SUM = SUM + SAMRAT(I)
C    FIND SAMPLE PER CENTS.
    DO 23 I = 1, 4
23   SAMPER(I) = SAMRAT(I)/ SUM
    IF( ISS(2)) 1003, 100, 1003
1003  WRITE OUTPUT TAPE 6, 2003, (SAMPER(I), I = 1, 4)
2003  FORMAT ( /10X, 23HUNSPIKED PER CENT 88 = F12.5, 10X, 23HUNSPIKED
1    PER CENT 87 = F12.5/ 10X, 23HUNSPIKED PER CENT 86 = F12.5, 10X,
2    23HUNSPIKED PER CENT 84 = F12.5 //)
C    PREPARE TO SOLVE FOR A BY ITERATION.
C    STEP 3, SOLVE FOR A.
100  A = (CONC(4)- RATIO(4)*CONC(3))/(RATIO(4)*SAMPER(3)-SAMPER(4))
C    STEP 4, FIND B, NUM(I), ANS(I).
    SUM = 0.
    DO 24 I = 1, 4
24   SUM = SUM + CONC(I)
    B = SUM + A
    DO 25 I = 1, 4
    ENUM(I) = PERCEN(I)*B
25   ANS(I) = ENUM(I) - CONC(I)
    IF( ISS(3)) 51, 50, 51
51   WRITE OUTPUT TAPE 6, 1504, (ENUM(I), I = 1, 4), SUM, B
1504  FORMAT( 10X, 19HTOTAL ISOTOPE 88 = F12.6, 2X, 10HMICROMOLES, 10X,
119HTOTAL ISOTOPE 87 = F12.6, 2X, 10HMICROMOLES/10X, 19HTOTAL ISOTOPE

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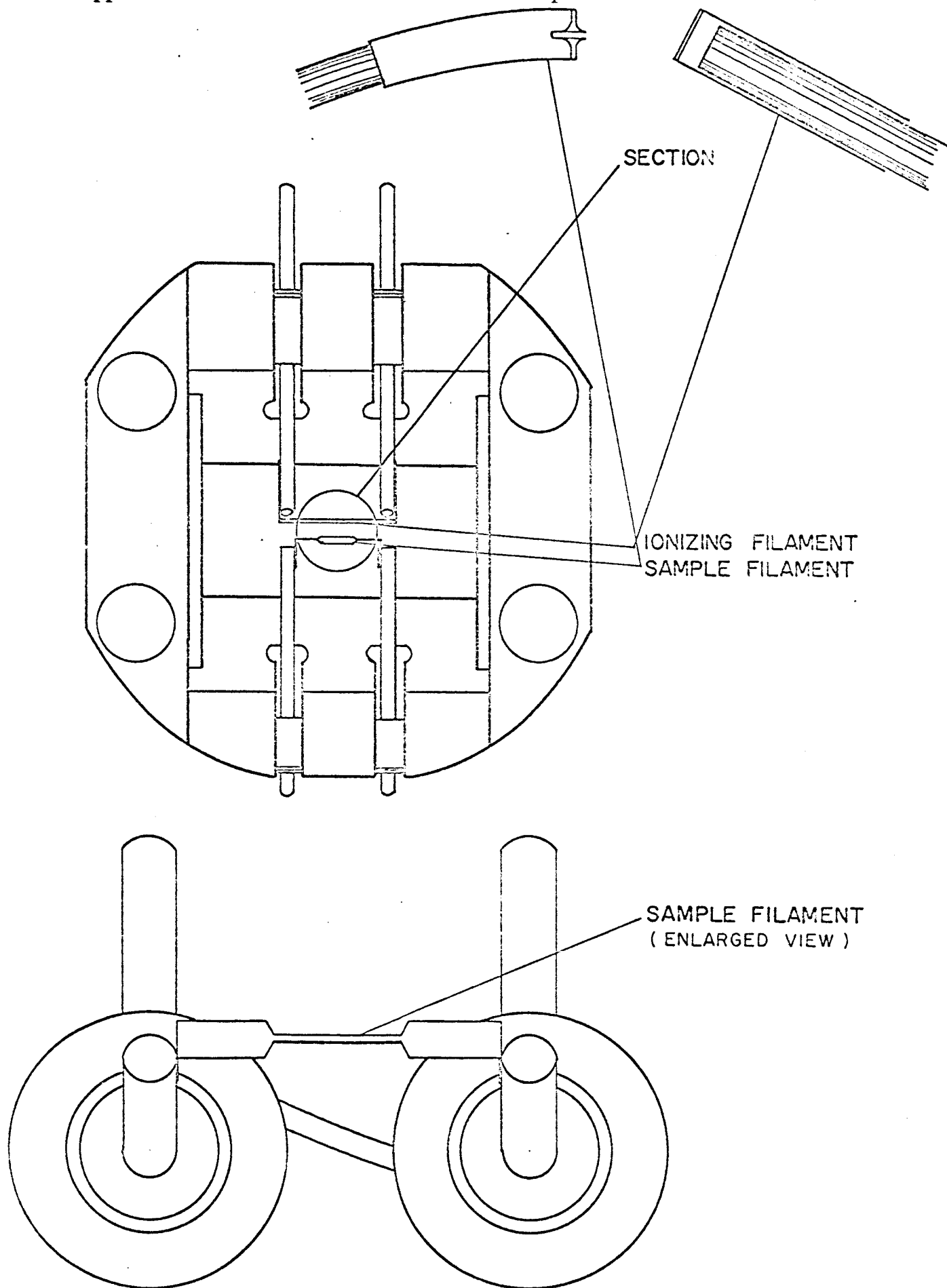
Appendix II (continued)

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286 = F12.6,2X,10HMICROMOLES,10X,19HTOTAL ISOTOPE 84 = F12.6,2X,
3 10HMICROMOLES/ 15HTOTAL TRACER = F12.6, 2X,
4 10HMICROMOLES, 10X, 38HTOTAL MICROMOLES
50F SAMPLE + TRACER = F12.6//)
WRITE OUTPUT TAPE 6, 503, (ANS(I), I = 1,4), A
C STEP 5, FIND TRIAL SAMPLE RATIOS.
50 DO 27 I = 1, 4
27 TRLS(I) = ANS(I) / ANS(3)
C STEP 6. FIND NEW RATIO(1), RATIO(2), RATIO(4) AND SAMRAT(2).
RATIO(1) = RATIO(1)*SAMRAT(1)/TRLS(1)
RATIO(2) = (0.5*((SAMRAT(1)/TRLS(1))-1.))+1.)*RATIO(2)
RATIO(4) = RATIO(4)*TRLS(1)/SAMRAT(1)
SAMRAT(2) = TRLS(2)*(0.5*((SAMRAT(1)/TRLS(1))-1.))+1.)
IF(ISS(3)) 5002, 5002, 5003
5003 WRITE OUTPUT TAPE 6, 15, (RATIO(I), I = 1,4)
WRITE OUTPUT TAPE 6, 16, (SAMRAT(I), I = 1,4)
5002 C1 = C
C = TRLS(1)/SAMRAT(1)
CI = SAMRAT(1)/TRLS(1)
IF( J - 2) 501, 500, 501
500 WRITE OUTPUT TAPE 6, 502, (TRLS(I), I = 1,4), C, CI
502 FORMAT (30X, 21HTRIAL UNSPIKED RATIOS/ 5X,
1 7H88/86 = F12.5, 5X, 7H87/86 = F12.5,5X,7H86/86 = F12.5,5X,7H84/8
26 = F12.5/ 5X,43HTRIAL RATIO 88/86 / UNSPIKED RATIO 88/86 =
3 F12.5, 5X, 43HUNSPIKED RATIO 88/86 / TRIAL RATIO 88/86 = F12.5 /)
501 J = J - 1
J1 = -J+2
C REPEAT A SECOND TIME.
IF ( J ) 101, 101,5000
101 IF (ISS(10))103,103,102
102 IF(ABS((C-C1)/C) - 0.0001 ) 103,103,104
104 IF (J1 - 10) 5000, 103, 103
103 WRITE OUTPUT TAPE 6, 503, (ANS(I), I = 1, 4), A
503 FORMAT ( 10X, 19HMICROMOLES SR 88 = F12.6, 5X, 19HMICROMOLES SR 87
1 = F12.6/10X,19HMICROMOLES SR 86 = F12.6, 5X, 19HMICROMOLES SR 84
2= F12.6/ 10X, 38HTOTAL UNSPIKED MICROMOLES OF SAMPLE = F12.6//)
C STEP 10. FIND ANS(I), A CORRECTED FOR WEIGHT.
DO 28 I = 1, 4
28 ANS(I) = ANS(I)/ WEIGHT
A = A/ WEIGHT
WRITE OUTPUT TAPE 6, 504
504 FORMAT ( 10X,34HANSWERS AND A CORRECTED FOR WEIGHT//)
WRITE OUTPUT TAPE 6, 503, (ANS(I), I = 1,4), A
DO 30 I = 1, 4
30 TRLS(I) = ANS(I)/ ANS(3)
C = TRLS(1) / SAMRAT(1)
CI = SAMRAT(1)/TRLS(1)
WRITE OUTPUT TAPE 6, 502,(TRLS(I), I = 1,4) , C , CI
RAB7 =-ORGRAT*ANS(3) +ANS(2)
WRITE OUTPUT TAPE 6, 1510, RAB7
1510 FORMAT ( 10X, 16HRADIOGENIC SR87 = F12.6,2X, 20HMICROMOLES PER GRA
1M./)
WRITE OUTPUT TAPE 6, 1511, (TITLE(J), J = 1,11), RAB7
1511 FORMAT (10A6,A2,F12.6)
WRITE OUTPUT TAPE 6, 1505 , J1
1505 FORMAT(10X, 21HANSWER HAS REQUIRED 12, 2X, 11HITERATIONS.)
GO TO 1
END
END

```


Appendix III. Filament holder for two-temperature surface ionization source.



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